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54 Aromatic polysulfone resin composition.

57 An aromatic polysulfone resin composition comprises 20 to 80% by weight of an aromatic polysulfone, 10 to 70% by weight of a fibrous reinforcement or an inorganic filler, and 0.5 to 20% by weight of a fluoro-resin. The aromatic polysulfone resin composition has heat resistance, strength, stiffness, flame resistance and processability superior to known sulfone resins and is particularly useful as an engineering plastics material.

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AROMATIC POLYSULFONE RESIN COMPOSITION

1 BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

This invention relates to an aromatic polysulfone resin composition exhibiting high heat resistance, superior mechanical properties, low mold shrinkage, and good mold releasability.

DESCRIPTION OF THE PRIOR ART

Aromatic polysulfone resins are noticed as engineering plastics superior in heat resistance, strength, stiffness, flame resistance, chemical resistance, processability, etc., particularly in the fields of applications to electric parts and automotive parts.

In these application fields, however, there is a growing need, with technical progress in these fields, for an aromatic polysulfone resin composition having higher heat resistance, stiffness, and dimensional accuracy (low mold shrinkage) while maintaining the flame resistance, chemical resistance, hot water resistance, and processability which are merits of this resin.

It is known that the heat resistance, stiffness, and dimensional accuracy of resins are improved, as a rule, by incorporating therein a fibrous reinforcement such as glass fiber, carbon fiber, or the like or an inorganic filler in powdery, acicular, or flaky form, such as talc, calcium carbonate, magnesium carbonate,

1 calcium sulfite, aluminum hydroxide, mica, molybdenum
disulfide, wollastonite, graphite, titanium white, or
glass beads.

Also when aromatic polysulfone resin is compounded
5 with such a reinforcement or filler, improvements in
the heat resistance and stiffness and a decrease in the
mold shrinkage are observed responsively to the quantity
of the reinforcement or filler blended.

With the increase of quantity of the reinforce-
10 ment or filler blended, the mold shrinkage decreases
and the mold fidelity in injection molding and in similar
molding becomes better; but the mold releasability in
injection molding lowers and the take-off of the molded
article from the mold cavity becomes difficult. In
15 consequence, excess stress is exerted on the molded
article when it is ejected from the cavity; this leaves
strain in the molded article and may cause troubles such
as the deformation of the molded article at the time of
the ejection and the stress cracking and eventual break
20 of the finished article.

Accordingly, in spite of the strong request
for a resin composition exhibiting low mold shrinkage
and excellent mold fidelity and dimensional accuracy,
the quantity of the reinforcement or filler to be blended
25 is usually restricted so as to hold the reduction of the
mold shrinkage in such a degree that none of the above
problems arise in the operation of releasing the molded
article from the mold cavity.

1 In view of the above, the present inventors
made intensive studies, and as a result, found that a
resin composition which has high heat resistance, stiffness,
and strength and exhibits low mold shrinkage and good
5 mold releasability can be obtained by compounding an
aromatic polysulfone with a fibrous reinforcement or an
inorganic filler and additionally with a specified amount
of a fluororesin. Based on this finding, this invention
has been accomplished.

10 SUMMARY OF THE INVENTION

An object of the present invention is to provide
an aromatic polysulfone resin composition excellent in
processability as well as in heat resistance, stiffness,
and strength.

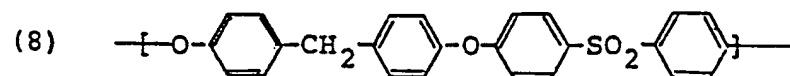
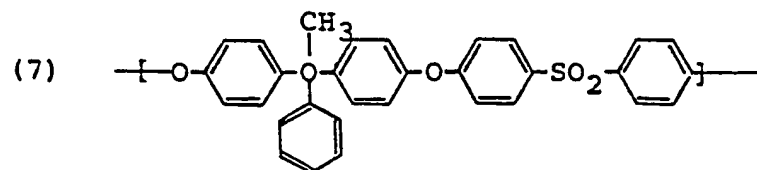
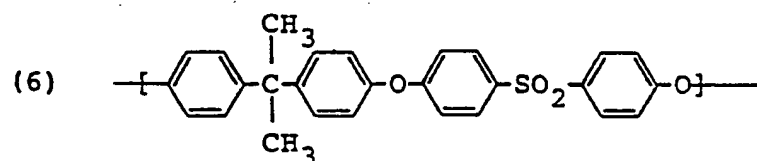
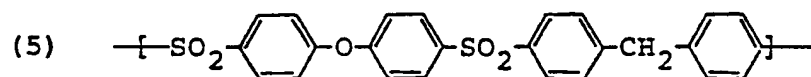
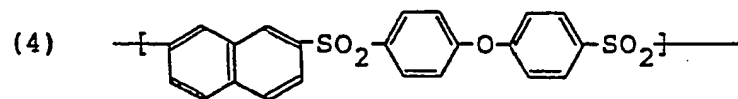
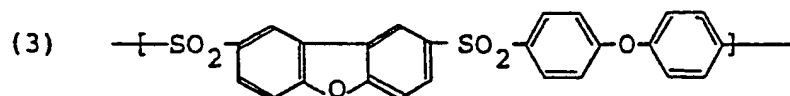
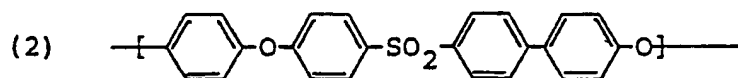
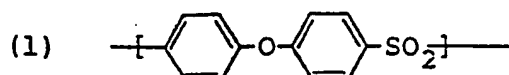
15 Other objects and advantages of the present
invention will be apparent from the following description.

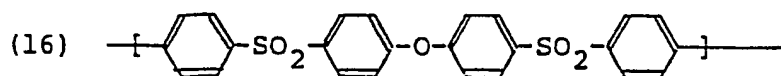
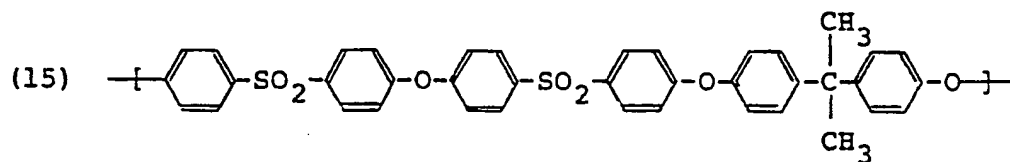
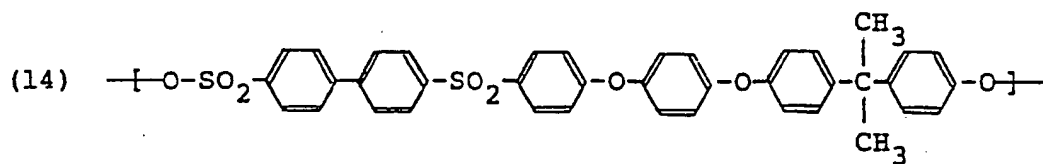
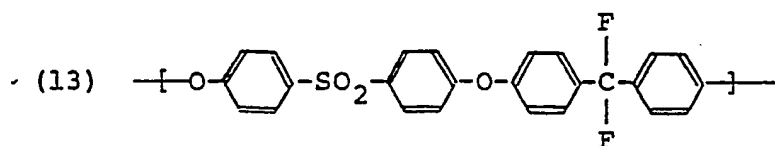
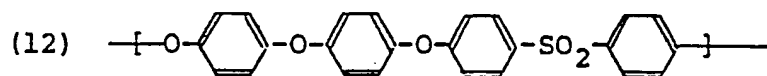
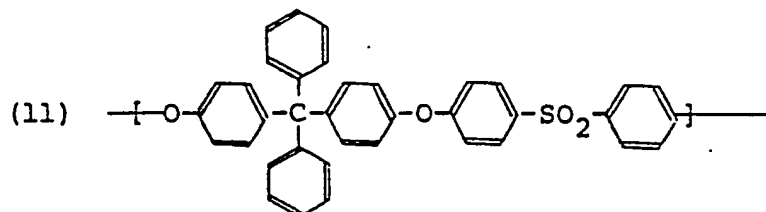
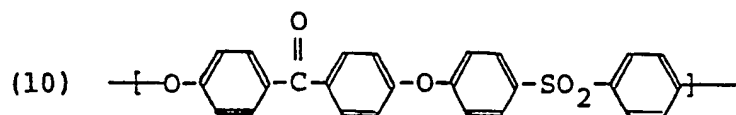
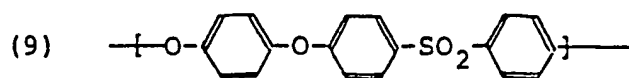
According to the present invention, there is
provided an aromatic polysulfone resin composition which
comprises 20 to 80% by weight of an aromatic polysulfone,
20 10 to 70% by weight of a fibrous reinforcement or an
inorganic filler, and 0.5 to 20% by weight of a fluoro-
resin.

DETAILED DESCRIPTION OF THE INVENTION

The aromatic polysulfone to be used as a
25 component of the composition of this invention may be
a polyarylene compound in which arylene units together

1 with ether linkages and with sulfone linkages are arranged
 orderly or disorderly. Polymers of the following structures
 (1) - (16) are given as examples of the aromatic poly-
 sulfone. Of these polymers, particularly preferred are
 5 those of the structures (1), (2), and (6) in that physical
 properties and processability thereof are well balanced.





1 Further, the aromatic polysulfones exhibiting
a reduced viscosity of 0.3 - 0.6, as determined at 25°C
on a 1 W/V % solution of the polymer in dimethylformamide,
are best suited because these are excellent in the balance
5 of physical properties such as heat resistance, stiffness,
and strength with processability.

Examples of the fibrous reinforcement used as
another component of the composition of this invention
are glass fiber, carbon fiber, aromatic polyamide fiber,
10 silicon carbide fiber, silicon nitride fiber, alumina
fiber, potassium titanate fiber, and mineral fibers; that
is, fibrous reinforcements generally used for improving
the heat resistance, strength, stiffness, etc. of resins
can also be used herein.

15 Examples of the inorganic filler used as another
component of the composition of this invention (additionally
or alternatively to the fibrous reinforcement) are talc,
calcium carbonate, magnesium carbonate, calcium sulfite,
aluminum hydroxide, mica, molybdenum disulfide, wollastonite,
20 graphite, titanium white, glass beads, zirconia, and silica.

These fibrous reinforcements and inorganic
fillers can be used normally as such without any treatment,
but also used after treatment thereof with a silane
coupling agent such as an aminosilane or an epoxysilane
25 or with chromic chloride for the purpose of enhancing
the affinity for the aromatic polysulfone, or with other
surface treating agents which meet individual purposes.

The fluororesin used as another component of

1 the composition of this invention is a macromolecular
compound containing fluorine atoms in the molecule.
Examples thereof are tetrafluoroethylene resin, tetra-
fluoroethylene-perchloroalkyl vinyl ether copolymer resin,
5 tetrafluoroethylene-hexafluoropropylene copolymer resin,
tetrafluoroethylene-ethylene copolymer resin, chloro-
trifluoroethylene resin, and vinylidene fluoride resin.

Of these fluororesins, tetrafluoroethylene
resin (polytetrafluoroethylene) is preferable for the
10 following reason: This polymer has a high melt viscosity
and hence hardly flows even when heated to temperatures
above its melting point (about 330°C). Therefore its
state of dispersion in the aromatic polysulfone is little
altered under the usual conditions of molding the resin
15 composition, so that characteristics, mechanical strengths,
and mold releasability in injection molding, of the
composition are scarcely varied by molding.

Suitable blending proportions of these components
of the composition are 20 to 80% by weight of the aromatic
20 polysulfone, 10 to 70% by weight of the fibrous reinforce-
ment or inorganic filler, and 0.5 to 20% by weight of
the fluororesin, based on the total weight of the com-
position, wherein the combined proportion of the fibrous
reinforcement or inorganic filler with the fluororesin
25 is desired to be in the range of 20 to 80% by weight.

When the combined proportion of the reinforce-
ment or filler with fluororesin is more than 80% by
weight and the proportion of the aromatic polysulfone is

1 less than 20% by weight, sufficient mixing of the components
is unattainable and the resulting composition is hence
nonuniform, loses fluidity, and is difficult to mold.
When the combined proportion of the reinforcement or
5 filler with the fluororesin is less than 20% by weight,
the sufficient effect of lowering mold shrinkage cannot
be obtained.

When the proportion of the reinforcement or
filler is less than 10% by weight, the effect of lowering
10 mold shrinkage is insufficient even if the combined
proportion of the reinforcement or filler with the fluoro-
resin is 20 to 80% by weight. On the other hand, when
the proportion of the fluororesin is less than 0.5% by
weight, the mold releasability in injection molding is
15 insufficient.

When the proportion of the reinforcement or
filler exceeds 70% by weight, the compounding becomes
difficult and insufficient, giving a nonuniform composi-
tion. When the proportion of the fluororesin exceeds 20%
20 by weight, the strength of the resulting composition
remarkably lowers.

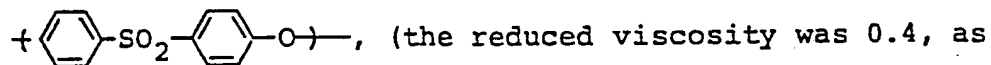
The blending method for the composition of this
invention is not particularly restricted. The aromatic
polysulfone, the fibrous reinforcement or inorganic filler,
25 and the fluororesin can be fed separately into a melt
mixer or may be mixed in a mortar, Henschel mixer, ball
mill, ribbon blender, or the like prior to the feeding
into a melt mixer.

1 One or more usual additives can be incorporated
into the composition of this invention unless departing
from the object of the invention. Such additives include
antioxidants, heat stabilizers, ultraviolet absorbers,
5 lubricants, mold releasing agents, colorants such as
dyes and pigments, flame retardants, auxiliary flame
retardants, antistatics, etc.

The invention is illustrated in more detail
with reference to the following examples; however, these
10 examples are intended not to restrict the invention but
to give preferred embodiments thereof.

Examples 1 to 5

A polyethersulfone having the basic structure



15 determined at 25°C on a 1 W/V % solution of the polymer
in dimethylformamide), wollastonite (CaSiO₃ in acicular
form, supplied by Nagase & Company, Ltd. under the
tradename of NYAD-G), and tetrafluoroethylene resin
(supplied by Imperial Chemical Industries Ltd. under the
20 tradename of Fluon L 169) were mixed in proportions as
shown in Table 1. The mixture was melted and mixed at
340°C by using a twin-screw extruder (PCM-30, supplied
by Ikegai Corporation). The resulting strands were cold
and cut into pellets.

25 Pellets thus obtained were injection-molded
(Sumitomo-Nestal 47/28 injection molding machine, cylinder

1 temperature 360°C, mold temperature 130°C) into bending
test specimens. After the mold was opened, the resistance
against the ejection of each molded part with the ejector
pin was measured by using a strain gage type of pressure
5 sensor.

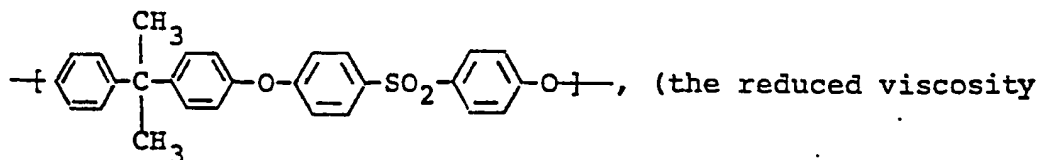
These bending test specimens were measured
for flexural strength, flexural modulus, heat deflection
temperature, and mold shrinkage. The flexural strength
and the heat deflection temperature were determined in
10 accordance with ASTM D-790 and ASTM D-648 (18.6 Kg/cm²),
respectively. The results were summarized in Table 1.

Comparative Examples 1 to 5

The same polyethersulfone, wollastonite, and
tetrafluoroethylene resin as used in Examples 1 to 5 were
15 mixed in proportions as shown in Table 1, and molded and
tested for physical properties in the same manner as in
Examples 1 to 5. The results are summarized in Table 1.

Examples 6 to 10

A polysulfone having the basic structure



was 0.38, as determined at 25°C on a 1 W/V % solution of
the polymer in dimethylformamide), glass fiber (REV-8,
supplied by Nihon Sheet Glass Co., Ltd.), and tetrafluoro-
ethylene resin (supplied by Daikin Industries, Ltd.

1 under the tradename of Lubron L-5) were mixed in proportions as shown in Table 2. The mixture was melted and mixed at 320°C by using a twin-screw extruder (PCM-30, supplied by Ikegai Corporation). The resulting strands
5 were cooled with water and cut into pellets.

Pellets thus obtained were injection-molded (Sumitomo-Nestal 47/28 injection molding machine, cylinder temperature 340°C, mold temperature 110°C) into bending test specimens. The resistance against the ejection,
10 flexural strength, flexural modulus, heat deflection temperature, and mold shrinkage were measured in the same manner as in Examples 1 to 5. The results are summarized in Table 2.

Comparative Examples 6 to 10

15 The same polysulfone, glass fiber and tetrafluoroethylene resin as used in Examples 6 to 10 were mixed in proportions as shown in Table 2 and molded and tested for physical properties in the same manner as in Examples 6 to 10. The results are summarized in Table 2.

Table 1

| | Composition | | | Resistance against ejection of injection-molded article (Kg/cm ²) | Mold shrinkage (%) | Flexural strength (kg/cm ²) | Flexural modulus (kg/cm ²) | Heat deflection temperature (°C) |
|-----------------------|--------------------|--------------|-------------|-------------------------------------------------------------------------------|-----------------------------------------------------------------------|-----------------------------------------|----------------------------------------|----------------------------------|
| | Poly-ether-sulfone | Wollastonite | Fluororesin | | | | | |
| Example 1 | 40 | 55 | 5 | 130 | 0.1 | 1100 | 120,000 | 215 |
| " | 50 | 45 | 5 | 100 | 0.2 | 1200 | 101,000 | 213 |
| " | 70 | 25 | 5 | 80 | 0.3 | 1300 | 85,000 | 210 |
| " | 50 | 49 | 1 | 105 | 0.2 | 1250 | 110,000 | 215 |
| " | 50 | 40 | 10 | 95 | 0.2 | 1150 | 90,000 | 212 |
| Comparative Example 1 | 100 | 0 | 0 | 250 | 0.7 | 1300 | 26,500 | 203 |
| " | 90 | 5 | 5 | 65 | 0.6 | 1300 | 27,000 | 205 |
| " | 10 | 85 | 5 | Molding was infeasible | | | | |
| " | 50 | 20 | 30 | 70 | 0.5 | 650 | 65,000 | 210 |
| " | 50 | 49.9 | 0.1 | 500 | Measurement was infeasible on account of cracks formed in molded part | | | |

Table 2

| | Composition | | | | Resistance against ejection of molded article (Kg/cm ²) | Mold shrinkage (%) | Flexural strength (Kg/cm ²) | Flexural modulus (Kg/cm ²) | Heat deflection temperature (°C) |
|-----------------------|--------------|-------------|--------------|--|---------------------------------------------------------------------|-----------------------------------------------------------------------|-----------------------------------------|----------------------------------------|----------------------------------|
| | Poly-sulfone | Glass fiber | Fluoro-resin | | | | | | |
| Example 6 | 40 | 55 | 5 | | 120 | 0.1 | 1000 | 135,000 | 185 |
| " 7 | 50 | 45 | 5 | | 95 | 0.2 | 1100 | 110,000 | 182 |
| " 8 | 70 | 25 | 5 | | 70 | 0.3 | 1200 | 100,000 | 180 |
| " 9 | 50 | 49 | 1 | | 100 | 0.2 | 1150 | 125,000 | 185 |
| " 10 | 50 | 40 | 10 | | 85 | 0.2 | 1050 | 105,000 | 183 |
| Comparative Example 6 | 100 | 0 | 0 | | 230 | 0.7 | 1100 | 26,500 | 174 |
| " 7 | 90 | 5 | 5 | | 60 | 0.6 | 1100 | 27,000 | 175 |
| " 8 | 10 | 85 | 5 | | Molding was infeasible | | | | |
| " 9 | 50 | 20 | 30 | | 65 | 0.5 | 500 | 70,000 | 180 |
| " 10 | 50 | 49.9 | 0.1 | | 450 | Measurement was infeasible on account of cracks formed in molded part | | | |

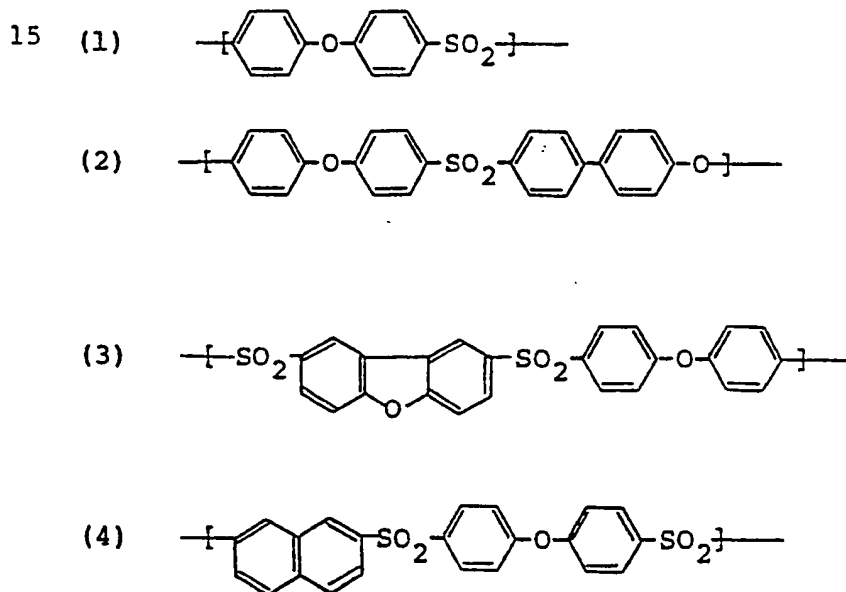
1 The following have been revealed from the above
examples and comparative examples.

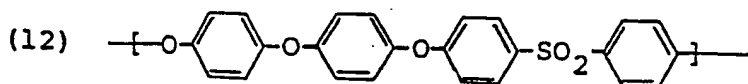
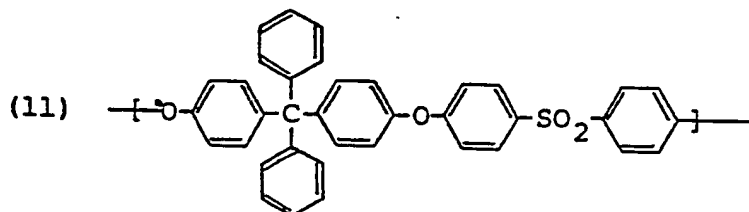
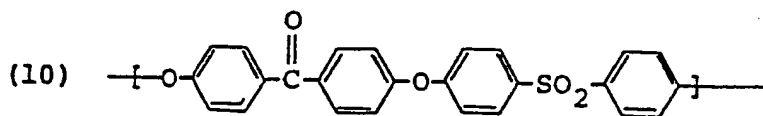
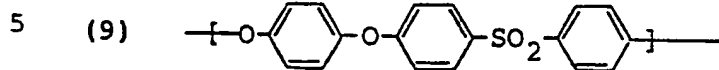
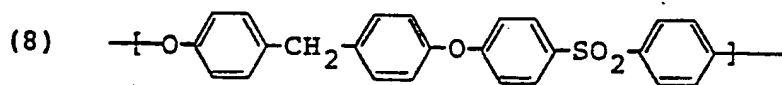
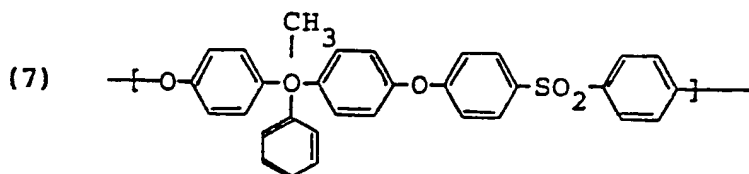
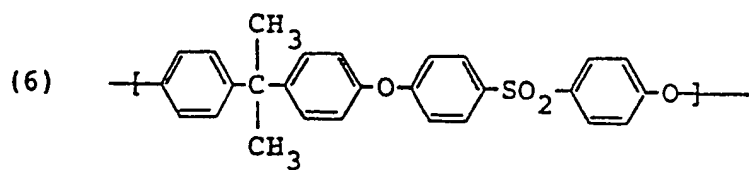
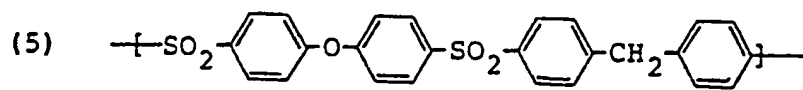
 The compositions according to the present
invention are improved in heat resistance and stiffness
5 (flexural modulus) as compared with the conventional
aromatic polysulfone resin compositions, and exhibit
high strength and additionally low mold shrinkage and
good mold releasability (Examples 1 to 10).

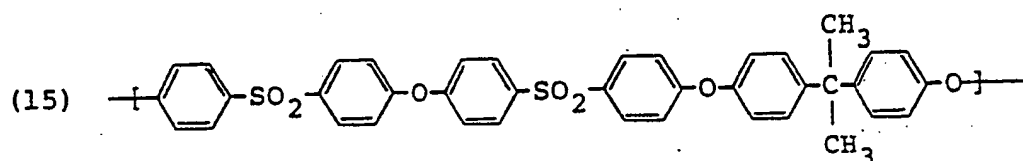
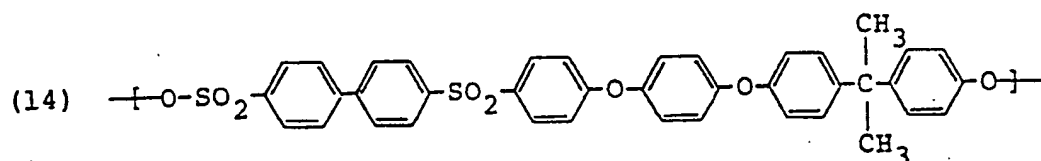
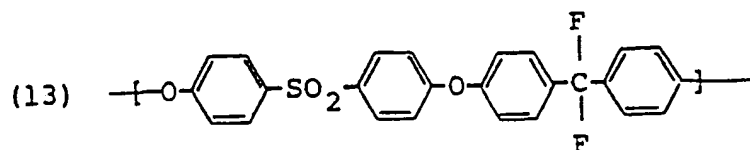
 The tested compositions except those of this
10 invention do not have the intended good properties, as
those (Comparative Examples 2 and 7) have been improved
insufficiently in mold shrinkage, those (Comparative
Examples 4 and 9) have much lowered strength, and those
(Comparative Examples 5 and 10) are unsatisfactory in
15 mold releasability.

WHAT IS CLAIMED IS:

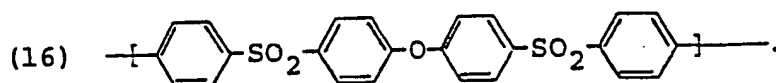
1. An aromatic polysulfone resin composition comprising 20 to 80% by weight of an aromatic polysulfone, 10 to 70% by weight of a fibrous reinforcement or an inorganic filler, and 0.5 to 20% by weight of a fluororesin, wherein the combined content of the fibrous reinforcement or inorganic filler with the fluororesin is 20 - 80% by weight based on the total weight of the composition.
2. The resin composition of Claim 1, wherein the aromatic polysulfone is a polyarylene compound including arylene units, ether linkages and sulfone linkages, the arylene units, sulfone linkages and ether linkages being arranged in any sequence.
3. The resin composition of Claim 2, wherein the aromatic polysulfone includes the structure:



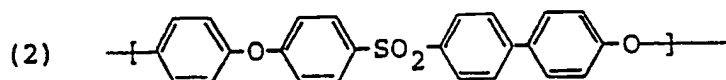
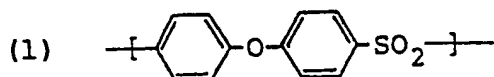




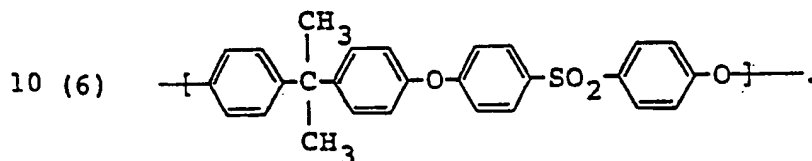
or



5 4. The resin composition of Claim 3, wherein the aromatic polysulfone has the structure:



or



5. The resin composition of any preceding Claim, wherein the reduced viscosity of the aromatic polysulfone is 0.3 to 0.6 as determined at 25°C on a 1 W/V % solution of the polymer in dimethylformamide.
- 5 6. The resin composition of any preceding Claim, wherein the fibrous reinforcement is at least one member selected from the group consisting of glass fiber, carbon fiber, aromatic polyamide fiber, silicon carbide fiber, silicon nitride fiber, alumina fiber, potassium titanate fiber
- 10 and mineral fiber.
7. The resin composition of any preceding Claim, wherein the inorganic filler is at least one member selected from the group consisting of talc, calcium carbonate, magnesium carbonate, calcium sulfite, aluminum hydroxide, mica,
- 15 molybdenum disulfide, wollastonite, graphite, titanium white, glass beads, zirconia, and silica.
8. The resin composition of any preceding Claim, wherein the fibrous reinforcement or the inorganic filler has been treated with a surface treating agent.
- 20 9. The resin composition of any preceding Claim, wherein the fluoro-resin is tetrafluoroethylene resin, tetrafluoroethylene-perchloroalkyl vinyl ether copolymer resin, tetrafluoroethylene-hexafluoropropylene copolymer resin, tetrafluoroethylene-ethylene copolymer resin, chloro-
- 25 trifluoroethylene resin, or vinylidene fluoride resin.
10. The resin composition of Claim 9, wherein the fluoro-resin is tetrafluoroethylene resin.



European Patent
Office

EUROPEAN SEARCH REPORT

0132094

Application number

EP 84 30 4646

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------|----------------------------------------------------------------------------------|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl. 4) |
| X | FR-A-2 378 056 (ICI) * Claims 1,9,15; page 11, lines 7-34; page 12, lines 5-12; example 3 * | 1-10 | C 08 K 3/00 C 08 K 7/02 C 08 L 81/06 (C 08 L 81/06 C 08 L 27/12) // |
| A | --- CHEMICAL ABSTRACTS, vol. 99, no. 2, 11th July 1983, page 32, no. 6521m, Columbus, Ohio, USA; & JP - A - 58 05358 (HITACHI LTD.) 12-01-1983 ----- | 6 | |
| | | | TECHNICAL FIELDS SEARCHED (Int. Cl. 4) |
| | | | C 08 K C 08 L |
| The present search report has been drawn up for all claims | | | |
| Place of search THE HAGUE | | Date of completion of the search 22-10-1984 | Examiner HOFFMANN K.W. |
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